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TITLE OF THE INVENTION

LIQUID PHASE GROWTH METHOD FOR SILICON CRYSTAL,
MANUFACTURING METHOD FOR SOLAR CELL AND LIQUID PHASE GROWTH
5 APPARATUS FOR SILICON CRYSTAL

BACKGROUND OF THE INVENTIONField of the Invention

10 [0001] The present invention relates to a liquid phase
growth method for a silicon crystal, a manufacturing method
for a solar cell and a liquid phase growth apparatus for a
silicon crystal. In particular, the present invention
relates to a liquid phase growth method for a silicon
15 crystal, the method capable of achieving continuous growth
and suitable for mass production, a manufacturing method for
a solar cell including the same and a liquid phase growth
apparatus for a silicon crystal, the apparatus used for
these methods.

20 Description of the Related Art

[0002] A liquid phase growth method has the advantage
that a high quality crystal having a composition close to
the stoichiometric composition can be prepared because of
crystal growth in a quasi-equilibrium state, and the method
25 is thereby used as an established technology with respect to

compound semiconductors, e.g., GaAs, for production of
light-emitting diodes (LEDs), laser diodes and the like.
Recently, liquid phase growth of Si has been attempted for
the purpose of preparing a thick film, and an application to
5 solar cells has been discussed, as disclosed in Japanese
Patent Laid-Open No. 58-89874.

[0003] In generally known liquid phase growth methods, a
solution containing a material targeted for growing, as a
solute, is cooled to become supersaturated and, thereby, an
10 excessive solute (a material targeted for growing) is
deposited on a substrate. At that time, the solute must be
dissolved into the solvent to saturation in advance of
deposition (growth) of the solute on the substrate.

[0004] Common methods for dissolving a solute in a
15 solvent include the case where a solute is mixed with a
solvent while the amount of the solute is adjusted to bring
about saturation at a dissolution temperature, followed by
heating, and the case where heating is performed while a
solvent is in contact with a large amount of (more than the
20 amount required for saturation) base material composed of
the solute, followed by keeping at a dissolution temperature
to bring about saturation. In the former case, a newly-
weighed solute is put into the solvent every time the growth
is terminated, or the solvent is replaced with a fresh
25 solvent including the solute. In the latter case, a base

material to become the solute is put into the solvent or is pulled out of the solvent before the growth or after the growth and, finally, the base material is consumed to cause troubles in putting in or pulling out or cause shortage in the amount of dissolution. Consequently, replacement with a fresh base material is required. In all cases, apparatuses are stopped or the growth is suspended in order to replenish when raw materials are run out, so that time loss occurs. As described above, known methods have problems with respect to mass production.

[0005] Lertes (DE No. 2238205) discloses a method for directly supplying a solute from a gas phase into a solvent, in which a SiH_4 gas (a raw material gas) is allowed to contact the solvent surface. However, in this case, the SiH_4 gas is allowed to two-dimensionally contacts the solvent surface, Si atoms generated by decomposition at the solvent surface diffuse into the solvent to reach the surface of a growth substrate and, thereby, supply of Si is achieved. Consequently, the amount of supply of Si is not sufficient for achieving a practical growth rate.

[0006] Japanese Patent Laid-Open No. 11-292693 discloses a liquid phase growth method for a silicon crystal and a manufacturing method for a solar cell including the same. In the liquid phase growth method for a silicon crystal, a raw material gas containing at least silicon atoms is blown

into a solvent, the raw material gas is decomposed while the silicon atoms are simultaneously dissolved into the above-described solvent and, thereby, the silicon atoms are supplied to the above-described solvent. Subsequently, a substrate is immersed in the solvent or is allowed to contact the solvent and, thereby, a silicon crystal is grown on the substrate. According to this proposition, the raw material can be continuously supplied in practice.

[0007] However, even in the liquid phase growth method disclosed in Japanese Patent Laid-Open No. 11-292693, the supply efficiency of the raw material and/or the dopant to the solvent must be improved in order to further increase the growth rate and to change a doping profile at will.

SUMMARY OF THE INVENTION

[0008] The present invention was made in consideration of the above-described problems. Accordingly, it is an object of the present invention to provide a liquid phase growth method for a silicon crystal, which can improve the supply efficiency of a raw material and/or a dopant to a solvent and which is simple and suitable for mass production, and to provide a manufacturing method for a solar cell including the same and a liquid phase growth apparatus for a silicon crystal, which is used for these methods.

[0009] In order to overcome the above-described problems, a liquid phase growth method for a silicon crystal according to the present invention, in which a silicon crystal is grown on a substrate by immersing the substrate in a solvent or allowing the substrate to contact the solvent, includes the step of supplying a gas containing a raw material and/or a dopant to the above-described solvent after at least a part of the above-described gas is decomposed by application of energy to the gas. In the present invention and the present specification, the raw material refers to a substance to become a raw material for a silicon crystal, and typical examples thereof include silanes and derivatives thereof, e.g., halogenated silanes and disilane.

[0010] A manufacturing method for a solar cell according to the present invention includes at least a step of forming a silicon layer by liquid phase growth, and further includes the step of supplying a gas containing a raw material and/or a dopant to a solvent after at least a part of the above-described gas is decomposed by application of energy to the gas.

[0011] A first liquid phase growth apparatus for a silicon crystal according to the present invention includes a device for holding a solvent to dissolve a raw material for silicon, a device for immersing a substrate in the solvent or allowing the substrate to contact the solvent, a

device for supplying a gas containing at least a raw material and/or a dopant to the above-described solvent and an energy application device upstream to the gas supply device in order to decompose at least a part of the above-described gas containing the raw material and/or the dopant.

[0012] A second liquid phase growth apparatus for a silicon crystal according to the present invention includes a solvent receiver for holding a solvent to dissolve silicon atoms, a raw material gas feed pipe having gas blowoff holes in the solvent held in the solvent receiver, an energy application chamber which is connected to the raw material gas feed pipe and which applies energy to a gas passing through the raw material gas feed pipe outside the solvent receiver, a wafer cassette which holds substrates and which can be put into the solvent and be pulled out of the solvent held in the solvent receiver at will and a heating device for heating the above-described solvent.

[0013] A third liquid phase growth apparatus for a silicon crystal according to the present invention includes a solvent receiver for holding a solvent to dissolve silicon atoms, a growth vessel for performing liquid phase growth on a substrate, a pipe for circulating the solvent between the solvent receiver and the growth vessel, a raw material gas feed pipe having gas blowoff holes in the solvent held in the above-described solvent receiver, an energy application

chamber which is connected to the raw material gas feed pipe and which applies energy to a gas passing through the raw material gas feed pipe outside the solvent receiver, a wafer cassette which holds substrates and which can be put into the solvent and be pulled out of the solvent held in the solvent receiver at will and a heating device for heating the above-described solvent.

[0014] A fourth liquid phase growth apparatus for a silicon crystal according to the present invention includes a solvent receiver for holding a solvent to dissolve silicon atoms, a pipe for circulating the solvent, the pipe having both ends connected to the solvent receiver and having an opening other than both the ends, a raw material gas feed pipe having gas blowoff holes in the solvent held in the solvent receiver, an energy application chamber which is connected to the raw material gas feed pipe and which applies energy to a gas passing through the raw material gas feed pipe outside the solvent receiver, a holding component for holding a substrate in order that the substrate is allowed to contact the solvent at the above-described opening and a heating device for heating the above-described solvent.

[0015] Further objects, features and advantages of the present invention will become apparent from the following description of the preferred embodiments with reference to

the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [0016] Fig. 1 is a sectional view schematically showing
an example of a liquid phase growth apparatus according to
the present invention.

10 [0017] Fig. 2 is a sectional view schematically showing
an example of a liquid phase growth apparatus according to
the present invention, in which dissolution of silicon and
liquid phase growth can be simultaneously performed.

15 [0018] Fig. 3 is a sectional view schematically showing
an example of a liquid phase growth apparatus according to
the present invention, in which a mechanical agitation
device is included.

20 [0019] Fig. 4 is a sectional view schematically showing
an example of a liquid phase growth apparatus according to
the present invention, in which a substrate and a solvent is
in contact with each other at an opening.

25 [0020] Fig. 5 is a sectional view schematically showing
an example of a liquid phase growth apparatus according to
the present invention, in which two energy application
devices are included.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] Embodiments of the present invention will be described below with reference to drawings. However, the present invention is not limited to these embodiments.

5 [0022] Fig. 1 is a sectional view schematically showing an example of a liquid phase growth apparatus used for a liquid phase growth method according to the present invention. In Fig. 1, reference numeral 101 denotes a wafer cassette, reference numeral 102 denotes a substrate (wafer),
10 reference numeral 103 denotes a solvent receiver (crucible), reference numeral 104 denotes a solvent (melt), reference numeral 105 denotes a reaction product gas, reference numeral 106 denotes a raw material gas feed pipe, reference numeral 107 denotes a reaction tube, reference numeral 108
15 denotes an electric furnace (heater) and reference numeral 112 denotes an energy application device connected to the raw material gas feed pipe 106. Reference numeral 109 denotes gas blowoff holes provided at the end portion of the raw material gas feed pipe 106, reference numeral 110
20 denotes a gate valve and reference numeral 111 denotes an exhaust hole.

[0023] The liquid phase growth method and the liquid phase growth apparatus of the present invention will be described below with reference to Fig. 1. As shown in Fig.
25 1, the solvent 104 made of a metal (hereafter referred to as

a "metal solvent") is filled in the solvent receiver (crucible) 103 made of carbon, the raw material gas feed pipe 106 is provided along the side wall and the bottom of the crucible 103. The energy application device 112 for decomposing a raw material gas and/or a dopant gas is provided upstream to the raw material gas feed pipe. The wafer cassette 101 carrying the wafers 102 is located above the crucible 103, and by the vertical movement thereof, the wafers 102 are immersed in the metal solvent 104 or the wafers 102 are pulled up from the metal solvent 104, so that a growth starting treatment / growth termination treatment is performed. Since the wafer cassette 101 is provided with a rotation mechanism as well, thicknesses of the growing film can be made uniform in the wafer surface and among the wafers by rotating the wafer cassette 101 during growth. The crucible 103, the raw material gas feed pipe 106 and the wafer cassette 101 are contained in the reaction tube 107, and are heated with the electric furnace 108 serving as a heating device disposed on the exterior of the reaction tube 107.

[0024] A specific procedure of the liquid phase growth method of the present invention will be described below. The metal solvent 104 not reached saturation or the metal solvent 104 after growth is terminated is heated to a predetermined temperature (a temperature slightly higher

than the temperature during growth), followed by keeping to stabilize.

[0025] A raw material gas, e.g., SiH_4 , as a supply source of Si, is fed into the raw material gas feed pipe 106

5 through the energy application device 112, and a decomposed raw material gas is injected into the metal solvent 104 from the gas blowoff holes 109 opened at the end portion of the raw material gas feed pipe 106, so that the decomposed raw material gas and the metal solvent 104 are allowed to

10 contact with each other. In the case where SiH_4 is used as the raw material gas and, for example, plasma discharge is used as the energy application device 112, SiH_4 is decomposed into SiH_3 , SiH_2 , SiH , Si , H_2 and the like, these are supplied into the metal solvent 104 through the raw material gas feed
15 pipe 106, and are immediately decomposed into Si atoms to dissolve into the metal solvent 104. At this time, the metal solvent 104 is agitated by H_2 molecules generated and, therefore, dissolution of Si atoms into the solvent is accelerated. However, an agitation mechanism (not shown in
20 the drawing) may be separately provided to intentionally agitate.

[0026] After the decomposed raw material gas is blown into the metal solvent 104 for a predetermined time, the raw material gas is stopped, and the electric furnace 108 is
25 controlled to perform gradual cooling. When the temperature

has reached the growth starting temperature, the wafer cassette 101 is moved downward, and the wafer 102 is immersed in the metal solvent 104. Preferably, the wafer cassette 101 is rotated at a speed of a few revolutions per minute during growth in order that the thickness of the growing film becomes uniform.

[0027] After a lapse of a predetermined growth time, the wafer cassette 101 is pulled up from the metal solvent 104, so that the growth is terminated. In the present embodiment, since the wafers 102 are arranged with a predetermined inclination in the wafer cassette 101, the metal solvent 104 hardly remains on the surface of the wafer at that point in time when the wafer 101 is pulled up from the metal solvent 104. However, the metal solvent 104 may slightly remain at the portion (support portion) where the wafer 102 and the wafer cassette 101 are in contact with each other. In this case, the remaining metal solvent 104 can be flung away by rotating the wafer cassette at a rotation speed of a few tens of revolutions per minute or more.

[0028] Subsequently, the wafer cassette 101 is pulled up into a preliminary chamber (not shown in the drawing) provided separately from the reaction tube 107, and the wafers 102 are replaced. The above-described steps are repeated and, thereby, the liquid phase growth can be continuously performed.

[0029] In the present invention, when the raw material gas and/or the dopant gas and the metal solvent are allowed to contact each other, and the raw material is continuously supplied into the solvent, energy can be applied to the raw material gas and/or the dopant gas in advance. Consequently, the decomposition efficiency is increased than ever, the supply efficient of the raw material and the dopant to the solvent is improved, and the suitability for mass production can be further improved.

[0030] In the present invention, the dopant concentration in the solvent can be adjusted by appropriately changing the ratio between the amounts of flow of the raw material gas and the dopant gas supplied. That is, the dopant concentration in the silicon layer grown in the solvent may be changed depending on the growth condition of the crystal. However, even in this case, the dopant concentration can be adjusted at a constant by controlling the ratio between the amounts of flow of the raw material gas and the dopant gas. Conversely, the dopant profile in the silicon layer can also be intentionally changed.

[0031] The materials suitable for use as the solvent receiver 103 to contain the metal solvent 104 used in the present invention and the wafer cassette 101 to support the wafers 102 are, primarily, high purity carbon, high purity quartz or the like. Likewise, the high purity carbon, the

high purity quartz or the like is suitable for use as the material for the raw material gas feed pipe 106 used in the present invention, and the high purity quartz is suitable for use as the material for the reaction tube 107.

- 5 [0032] Examples of raw materials (raw material gases) suitable for use include, for example, silanes represented by $\text{Si}_n\text{H}_{2n+2}$ (where n represents a natural number), e.g., SiH_4 and Si_2H_6 , and halogenated silanes, e.g., SiH_2Cl_2 , SiHCl_3 , SiCl_4 , SiH_2F_2 and SiH_2F_6 . Examples of dopants (typically, doping gases supplied by addition to the raw material gas, although may be supplied separately from the raw material gas, as a matter of course) suitable for use include, for example, PH_3 , PF_3 , AsH_3 , SbH_3 , B_2H_6 , BF_3 , BCl_3 , $\text{Ga}(\text{CH}_3)_3$ and $\text{Ga}(\text{C}_2\text{H}_5)_3$.
- 10
- 15 [0033] Preferably, hydrogen (H_2) is added to the above-described raw material gas in order to serve as a carrier gas or to establish a reducing atmosphere for accelerating growth of the crystal. The ratio of the amount of the above-described raw material gas to that of hydrogen (H_2) is
- 20 appropriately determined in accordance with a forming method, the type of the raw material gas and, furthermore, the condition of the formation. However, the ratio between the amounts of feed flow is preferably 1 : 1,000 or more and 100 : 1 or less, and more preferably, is 1 : 100 or more and
- 25 10 : 1 or less.

[0034] The energy application device 112 used in the present invention is selected from heat, plasma, a catalyst and light. With respect to the heat, those like a quartz reactor provided with a heater on the exterior are suitable for use. In the case where the plasma serves as the energy application device, those like a common plasma CVD apparatus provided with a discharge device and a reaction chamber are suitable for use. In the case where the catalyst is used, those having a structure in which the raw material gas and/or the doping gas is blown on a tungsten wire allowed to become red-hot by passing current are suitable for use. In the case where the light is used, those like the quartz reactor are suitable for use in order that the raw material gas and/or the doping gas can be irradiated with light (primarily, ultraviolet light) through them (those like the quartz reactor) while a large optical absorption coefficient of the raw material gas and/or the doping gas is exhibited with respect to the light. In the case where the plasma or the light is used, as necessary, other atoms or molecules may be fed into the reaction chamber in order to efficiently transfer the above-described energy to the raw material gas and/or the doping gas. These atoms or molecules temporally absorb the plasma or optical energy, and transfer the energy to the raw material gas and/or the doping gas so as to decompose the raw material gas and/or the doping gas. A

very small amount of mercury vapor, an argon gas, a H₂ gas and the like are suitable for use as the above-described energy mediation material.

[0035] The decomposition efficiency of the raw material gas and/or the doping gas can be improved with the energy application device 112 of the present invention by within the range of several percent to several tens percent (40% or more) although the extent thereof is changed depending on the type and the configuration of the energy application device 112 to be used.

[0036] Examples of solvents suitable for use in the present invention include metal solvents made of In, Sn, Bi, Ga, Sb and the like. Epitaxial growth is performed by allowing the solvent and decomposed raw material gas and/or doping gas to contact with each other to dissolve Si atoms and/or dopants into the solvent, followed by gradually cooling the solvent, or by allowing the solvent to have a temperature gradient therein while Si atoms and/or dopants are supplied into the solvent from decomposed raw material gas and/or doping gas.

[0037] The temperature and the pressure in the liquid phase growth method used in the present invention are changed depending on the forming method, the type of the raw material (gas) to be used and the like. However, for example, in the case where silicon is grown by using Sn or

In as the solvent, the temperature of the solvent is desirably controlled at 600°C or more and 1,050°C or less. Preferably, the pressure is about 10^{-2} Torr to 760 Torr, and more preferably, is within the range of 10^{-1} Torr to 760 Torr.

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EXAMPLES

[0038] The growth of a desired crystal by the liquid phase growth method of the present invention will be described below in detail with reference to examples.

10 However, the present invention is not specifically limited to these examples.

[EXAMPLE 1]

[0039] In Example 1, an epitaxial layer of Si was grown through the use of a liquid phase growth apparatus having the configuration shown in Fig. 1. A solvent was In, and a raw material gas was SiH_4 . A wafer cassette 101 carrying five 5"-Si wafers 102 was arranged in a preliminary chamber (not shown in the drawing) and, therefore, was in a standby state. A solvent receiver 103 containing the In solvent 104 was heated with a heater 108, and the temperature of the solvent was maintained at a constant 960°C. Here, 5" refers to that the diameter of the wafer is 5 inches.

[0040] A gate valve 110 was opened. The wafer cassette 101 on standby in the preliminary chamber was put in the reaction tube 107, and was held directly above the solvent

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receiver 103. The gate valve 110 was kept open during the following steps.

[0041] The raw material gas SiH_4 and a H_2 gas (a ratio of the amounts of gas flow of $\text{SiH}_4 : \text{H}_2 = 1 : 20$) were fed into a raw material gas feed pipe 106 through an energy application device 112 (a plasma reaction chamber), and were injected into the In solvent 104. These gases were kept on flowing for 20 minutes. With respect to the plasma condition, discharge power of 350 W was applied between opposed electrodes at atmospheric pressure.

[0042] After the required gas was flowed, gradual cooling of the solvent in the reaction tube 107 was started at a rate of $-1^\circ\text{C}/\text{min}$ while the electric furnace 108 was controlled. When the temperature of the In solvent 104 reached 950°C , the wafer cassette 101 was moved down while being rotated at a rotation speed of 10 rpm, and was put into the In solvent 104. When the wafer cassette 101 was completely immersed in the In solvent 104, the downward movement was stopped, and liquid phase growth was performed for 60 minutes while the wafer cassette 101 was rotated at the same location.

[0043] Subsequently, the wafer cassette 101 was pulled up from the In solvent 104, and was suspended directly above the solvent receiver 103. The rotation speed was increased to 120 rpm and, thereby, a part of In remaining on the wafer

cassette was flung away, so that the liquid phase growth was completed.

[0044] The cross section of the grown epitaxial silicon layer was observed with a scanning electron microscope and a transmission electron microscope. As a result, it was verified that the thickness of the grown epitaxial silicon layer was about 15 μm and the crystallinity was excellent.

[COMPARATIVE EXAMPLE 1]

[0045] For purposes of comparison, the raw material gas was injected into the In solvent 104 under the same condition as that in Example 1 except that the energy application device 112 was not used. Sufficient amount was unable to supply into the In solvent in the period of 20 minutes, and 30 minutes or more were required to saturate the solvent with Si.

[EXAMPLE 2]

[0046] In Example 2, an epitaxial layer of Si was grown and impurity doping was simultaneously performed through the use of the liquid phase growth apparatus having the configuration shown in Fig. 1. A solvent was In, a raw material gas was SiH_4 , and the impurity doping gas was B_2H_6 . The wafer cassette 101 carrying five 5"-Si wafers 102 was arranged in the preliminary chamber (not shown in the drawing) and, therefore, was in a standby state. The solvent receiver 103 containing the In solvent 104 was

heated with an electric furnace 108, and the temperature of the solvent was maintained at a constant 960°C.

[0047] The gate valve 110 was opened. The wafer cassette 101 on standby in the preliminary chamber was put in the reaction tube 107, and was held directly above the solvent receiver 103. The gate valve 110 was kept open during the following steps.

[0048] The raw material gas SiH_4 , the doping gas B_2H_6 and a H_2 gas (a ratio of the amounts of gas flow of $\text{SiH}_4 : \text{H}_2 = 1 : 20$ and $\text{B}_2\text{H}_6/\text{SiH}_4 = 0.01$) were fed into the raw material gas feed pipe 106 through the energy application device 112 (a plasma reaction chamber), and were injected into the In solvent 104. These gases were kept on flowing for 20 minutes. With respect to the plasma condition, discharge power of 350 W was applied between the opposed electrodes at atmospheric pressure.

[0049] After the required gas was flowed, gradual cooling of the solvent in the reaction tube 107 was started at a rate of $-1^\circ\text{C}/\text{min}$ while the electric furnace 108 was controlled. When the temperature of the In solvent 104 reached 950°C, the wafer cassette 101 was moved down while being rotated at a rotation speed of 10 rpm, and was put into the In solvent 104. When the wafer cassette 101 was completely immersed in the In solvent 104, the downward movement was stopped, and liquid phase growth was performed

for 60 minutes while the wafer cassette 101 was rotated at the same location.

[0050] Subsequently, the wafer cassette 101 was pulled up from the In solvent 104, and was suspended directly above the solvent receiver 103. The rotation speed was increased to 120 rpm and, thereby, a part of In remaining on the wafer cassette was flung away, so that the liquid phase growth was completed.

[0051] The cross section of the grown epitaxial silicon layer was observed with a scanning electron microscope and a transmission electron microscope. As a result, it was verified that the thickness of the grown epitaxial silicon layer was about 15 μm and the crystallinity was excellent.

[COMPARATIVE EXAMPLE 2]

[0052] For purposes of comparison, the raw material gas was injected into the In solvent 104 under the same condition as that in Example 2 except that the energy application device 112 was not used. Sufficient amount was unable to supply into the In solvent in the period of 20 minutes, and 30 minutes or more were required to saturate the solvent with Si.

[0053] Comparisons were made between the amount of the impurities (dopants) B contained in a silicon layer grown through the use of the energy application device 112 and that contained in a silicon layer grown through the use of

no energy application device 112 by secondary ion mass spectrometry. In the case where the energy application device was used, the concentration of detected B was about two orders of magnitude higher than that in the other case.

5 In this manner, it was made clear that the efficiency of doping to the grown silicon layer was improved than ever by the liquid phase growth method of the present invention.

[EXAMPLE 3]

10 [0054] In Example 3, an epitaxial layer of Si was grown and impurity doping was simultaneously performed through the use of a liquid phase growth apparatus having the configuration shown in Fig. 5. A solvent was In, a raw material gas was SiH_4 and an impurity doping gas was PH_3 . A wafer cassette 501 carrying five 5"-Si wafers 502 was
15 arranged in a preliminary chamber (not shown in the drawing) and, therefore, was in a standby state. A solvent receiver 503 containing the In solvent 504 was heated with a heater 508, and the temperature of the solvent was maintained at a constant 960°C.

20 [0055] The gate valve 510 was opened. The wafer cassette 501 on standby in the preliminary chamber was put in a reaction tube 507, and was held directly above the solvent receiver 503. The gate valve was kept open during the following steps.

25 [0056] The raw material gas SiH_4 and a H_2 gas (a ratio of

the amounts of gas flow of $\text{SiH}_4 : \text{H}_2 = 1 : 20$) were fed into the raw material gas feed pipe 506 through the energy application device 512 (a plasma reaction chamber), the doping gas PH_3 and a H_2 gas (a ratio of the amounts of gas flow of $\text{PH}_3 : \text{H}_2 = 1 : 10$, and a ratio of the amounts of gas flow of $\text{PH}_3/\text{SiH}_4 = 0.01$ after PH_3 and SiH_4 were joined) were fed into the raw material gas feed pipe 506 through the energy application device 513 (a plasma reaction chamber), and were injected into the In solvent 504. These gases were kept on flowing for 20 minutes. With respect to the plasma condition of both of the energy application device 512 (the raw material gas SiH_4 + the H_2 gas) and the energy application device 513 (the doping gas PH_3 + the H_2 gas), discharge power of 350 W was applied between the opposed electrodes at atmospheric pressure.

[0057] After the required gas was flowed, gradual cooling of the solvent in the reaction tube 507 was started at a rate of $-1^\circ\text{C}/\text{min}$ while the electric furnace 508 was controlled. When the temperature of the In solvent 504 reached 950°C , the wafer cassette 501 was moved down while being rotated at a rotation speed of 10 rpm, and was put into the In solvent 504. When the wafer cassette 501 was completely immersed in the In solvent 504, the downward movement was stopped, and liquid phase growth was performed for 60 minutes while the wafer cassette 501 was rotated at

the same location.

[0058] Subsequently, the wafer cassette 501 was pulled up from the In solvent 504, and was suspended directly above the solvent receiver 503. The rotation speed was increased to 120 rpm and, thereby, a part of In remaining on the wafer cassette was flung away, so that the liquid phase growth was completed.

[0059] The cross section of the grown epitaxial silicon layer was observed with a scanning electron microscope and a transmission electron microscope. As a result, it was verified that the thickness of the grown epitaxial silicon layer was about 15 μm and the crystallinity was excellent.

[0060] A silicon layer was grown under the same condition as that described above except that the plasma condition of the energy application device 513 was changed (the discharge power was changed to 20 W). The amount of impurities (dopants) P contained in the silicon layer grown while the plasma conditions of the energy application device 512 and the energy application device 513 were adjusted to be the same (the discharge power was 350 W) and that contained in the silicon layer grown while the plasma conditions of the energy application device 512 and the energy application device 513 were adjusted to be different from each other (the discharge power of the 512 was 350 W, and the discharge power of the 513 was 20 W) were compared by secondary ion

mass spectrometry. As a result, the concentration of detected P in the former case was about three orders of magnitude higher than that in the latter case. In this manner, according to the liquid phase growth method of the present invention, the concentration of doping to the grown silicon layer can be easily controlled, and a doping profile can be achieved in a wide range.

[Example 4]

[0061] In Example 4, an epitaxial layer of Si was grown through the use of a liquid phase growth apparatus having the configuration shown in Fig. 3 and concurrent use of mechanical agitation devices (agitation mechanisms) for dissolving a solute in a solvent. The solvent was In, and a raw material gas was SiH_2Cl_2 . The agitation mechanisms were arranged in a preliminary chamber (not shown in the drawing) and, therefore, were in a standby state. A solvent receiver 303 containing the In solvent 304 was heated with an electric furnace 308, and the temperature of the solvent was maintained at a constant 960°C .

[0062] A gate valve 310 was opened. The agitation mechanisms 312 on standby in the preliminary chamber were put in the reaction tube 307, and was held directly above the solvent receiver 303. The gate valve was kept open during the following steps.

[0063] The raw material gas SiH_2Cl_2 and a H_2 gas (a ratio

of the amounts of gas flow of SiH_2Cl_2 : H_2 = 1 : 100) were fed into a raw material gas feed pipe 306 through an energy application device 314 (a quartz reactor provided with a heater on the exterior), and were injected into the In solvent 304. At this time, the heater temperature of the energy application device 314 was adjusted at 1,050°C.

[0064] The agitation mechanisms 312 were moved down while being rotated at a rotation speed of 20 rpm, and was put into the In solvent 304. When the impellers 313 were sufficiently immersed in the In solvent, the downward movement was stopped, and the gas was kept on flowing for 15 minutes while the impellers 313 were kept at the same location and agitation was performed.

[0065] After the required gas was flowed, the agitation mechanisms 312 were pulled up to the preliminary chamber. Subsequently, a wafer cassette 301 carrying five 5"-Si wafers 302 was put in the reaction tube 307 from the preliminary chamber, and was held directly above the solvent receiver 303 for 10 minutes.

[0066] Gradual cooling of the solvent in the reaction tube 307 was started at a rate of -1.5°C/min while the electric furnace 308 was controlled. When the temperature of the In solvent 304 reached 950°C, the wafer cassette 301 was moved down while being rotated at a rotation speed of 10 rpm, and was put into the In solvent 304. When the wafer

cassette 301 was completely immersed in the In solvent 304, the downward movement was stopped, and liquid phase growth was performed for 45 minutes while the wafer cassette 301 was rotated at the same location.

5 [0067] Subsequently, the wafer cassette 301 was pulled up from the In solvent 304, and was suspended directly above the solvent receiver 303. The rotation speed was increased to 120 rpm and, thereby, a part of In remaining on the wafer cassette was flung away, so that the liquid phase growth was
10 completed. In Fig. 3, reference numeral 305 denotes a reaction product gas, reference numeral 309 denotes a gas blowoff hole and reference numeral 311 denotes an exhaust hole.

15 [0068] The cross section of the grown epitaxial silicon layer was observed with a scanning electron microscope and a transmission electron microscope. As a result, it was verified that the thickness of the grown epitaxial silicon layer was about 15 μm and the crystallinity was excellent.

[COMPARATIVE EXAMPLE 3]

20 [0069] For purposes of comparison, the raw material gas was injected into the In solvent 304 under the same condition as that in Example 4 except that the energy application device 314 was not used. Sufficient amount was
25 unable to supply to the In solvent in the period of 15 minutes, and 20 minutes or more were required to saturate

the solvent with Si.

[EXAMPLE 5]

[0070] In Example 5, an epitaxial layer of Si was grown through the use of a liquid phase growth apparatus shown in Fig. 2. A solvent was Sn, and a raw material gas was SiH₄.

[0071] With respect to the apparatus shown in Fig. 2, a quartz solvent receiver 214 and quartz pipes 209a, 210 and 209b are disposed in an electric furnace 207, while the pipe 209a is connected to one side surface of the solvent receiver 214 and a growth vessel 203 for immersing a wafer cassette 201 carrying substrates (wafers) 202, the pipe 210 is connected to the growth vessel 203, and the pipe 209b is connected to the other side surface of the solvent receiver 214. The pipes 209a and 209b serve as heat exchangers.

Furthermore, the solvent receiver 214 and the heat exchanger 209b are surrounded by a heater block 208 and, therefore, the temperature can be controlled separately. Reference numeral 211 denotes a circulation rotor, reference numeral 212 denotes a gate valve, reference numeral 215 denotes an energy application device, reference numeral 206 denotes a raw material gas feed pipe and reference numeral 213 denotes an exhaust hole. Reference numeral 204 denotes a solvent and reference numeral 205 denotes a reaction product gas.

[0072] The solvent 204 was Sn sufficiently purified in a hydrogen atmosphere. The solvent 204 was filled in the

solvent receiver 214, the growth vessel 203 and the quartz pipes 209a, 210 and 209b. The temperature in the electric furnace 207 was maintained at a constant 950°C. The temperature of the solvent receiver 214 was adjusted by the heater block 208 at 10°C higher than the temperature in the electric furnace 207 outside the heater block 208, and the solvent 204 was circulated through the use of the rotor 211.

[0073] After a lapse of sufficient time, the gate valve 212 was opened. The wafer cassette 201 carrying beforehand five 5"-p⁺(100) Si wafers (wafers which were doped with relatively many p-type dopants and in which a principal plane had (100) plane orientation) 202 was put in the growth vessel 203 from a preliminary chamber (not shown in the drawing), and was held directly above the Sn solvent receiver 204. The raw material gas SiH₄ and a H₂ gas (a ratio of the amounts of gas flow of SiH₄ : H₂ = 1 : 30) were fed into the raw material gas feed pipe 206 through the energy application device 215 (a reaction chamber provided with a tungsten wire), and were injected into the Sn solvent 204 in the solvent receiver 214. These gases were kept on flowing. At this time, current was passed through the tungsten wire to heat the wire to 1,600°C, and the raw material gas SiH₄ and the H₂ gas was blown onto the heated wire.

[0074] After a lapse of 20 minutes, the wafer cassette

201 was moved down while being rotated at a rotation speed of 10 rpm, and was put into the Sn solvent 204 in the growth vessel 203. When the wafer cassette 201 was completely immersed in the Sn solvent 204, the downward movement was
5 stopped, and liquid phase growth was performed for 60 minutes while the wafer cassette 201 was rotated at the same location.

[0075] The wafer cassette 201 was pulled up from the Sn solvent 204, and was suspended directly above the Sn solvent
10 204. The rotation speed was increased to 150 rpm and, thereby, a part of Sn remaining on the wafer cassette 201 was flung away, so that the liquid phase growth was completed.

[0076] The cross section of the grown epitaxial silicon
15 layer was observed with a scanning electron microscope and a transmission electron microscope. As a result, it was verified that the thickness of the grown epitaxial silicon layer was about 20 μm and the crystallinity was excellent.

[COMPARATIVE EXAMPLE 4]

[0077] For purposes of comparison, the liquid phase
20 growth was performed under the same condition as that in Example 5 except that the energy application device 215 was not used. The thickness of the grown epitaxial silicon layer was in the order of 15 μm . Consequently, the grown
25 film had a larger thickness when the above-described energy

application device 215 was used.

[EXAMPLE 6]

[0078] In Example 6, a Si layer was grown on a polycrystalline Si substrate through the use of an apparatus shown in Fig. 4. A solvent was In + Ga (Ga content: 0.1 atomic percent), and a raw material gas was Si_2H_6 . Cast polycrystalline Si was processed to have a width of 40 mm, a length of 250 mm and a thickness of 0.6 mm, and was subjected to surface-polishing, followed by cleaning, in order to serve as the substrate.

[0079] With respect to the apparatus shown in Fig. 4, a solvent receiver 414 made of carbon and flat pipes 409a, 410 and 409b made of carbon are disposed in an electric furnace 407, while the 409a is connected to one side surface of the solvent receiver 414, the pipe 410 is in contact with a slider 402 carrying a plurality of substrates 401 at an opening 403, and the pipe 409b is connected to the other side surface of the solvent receiver 414. The pipes 409a and 409b serve as heat exchangers. Furthermore, the solvent receiver 414 and the heat exchanger 409b are surrounded by a heater block 408 and, therefore, the temperature can be controlled separately. Reference numeral 411 denotes a circulation rotor, reference numeral 415 denotes an energy application device, reference numeral 406 denotes a raw material gas feed pipe and reference numeral 413 denotes an

exhaust hole. Reference numeral 404 denotes a solvent and reference numeral 405 denotes a reaction product gas.

[0080] The solvent 404 was In + Ga sufficiently purified in a hydrogen atmosphere. The solvent 404 was filled in the solvent receiver 414 and the flat pipes 409a, 410 and 409b. The location of the slider 402 was adjusted beforehand in order that the Si substrate 401 was not become in contact with the solvent 404 at the opening 403 of the flat pipe. The temperature in the electric furnace 407 was maintained at a constant 950°C and, simultaneously, the temperature of the solvent receiver 414 was adjusted by the heater block 408 at 10°C higher than the temperature in the electric furnace 407 outside the heater block 408. Subsequently, the solvent 404 was circulated through the use of the rotor 411. At this time, the length of the opening 403 was adjusted to be 100 mm, and the circulation velocity of the solvent 404 was adjusted at 40 mm/min. In the present Example, three Si substrates were arranged on the slider.

[0081] The raw material gas Si_2H_6 was fed into the raw material gas feed pipe 406 through the energy application device 415 (a synthetic quartz reaction chamber provided with an ultraviolet light (UV) irradiation apparatus), and was injected into the In + Ga solvent 404. The gas was kept on flowing. At this time, in the synthetic quartz reaction chamber, the raw material gas Si_2H_6 was irradiated with the

UV (output 32 W: pulse energy 180 mJ) from an ArF excimer laser at a wavelength of 193 nm. After a lapse of 30 minutes, the polycrystalline Si substrate 401 was allowed to contact the In + Ga solvent 404 at the opening 403 while the slider 402 was moved at a feed speed of 20 mm/min and thereby, liquid phase growth was performed. When all of the plurality of polycrystalline Si substrates 401 passed through the opening 403, the movement of the slider 402 was stopped, so that the liquid phase growth was completed.

[0082] The cross section of the grown Si layer was observed with a scanning electron microscope and a transmission electron microscope. As a result, it was verified that the thickness of the grown Si layer was about 20 μm . The orientation of the grown Si layer was examined by an electron channeling pattern (ECP) method, and it was made clear that the crystal orientation of each grain in the polycrystalline Si substrate serving as a base material was followed. As described above, the crystalline Si layer was able to continuously grow while the substrate was moved.

[0083] In the case shown in Example 6, the substrate arranged on the slider was used. However, for example, it is also possible that a web-like substrate provided with an Si layer adhered to the surface is allowed to contact a solvent, and the Si layer is continuously grown while the substrate is moved roll-to-roll in one direction.

[EXAMPLE 7]

[0084] In Example 7, an n⁺/p type thin-film single-crystal solar cell was prepared through the use of the liquid phase growth method of the present invention.

5 [0085] The apparatus shown in Fig. 1 was used, and an epitaxial Si layer was grown on a p⁺ Si wafer ($\rho = 0.01 \Omega \cdot \text{cm}$) having a thickness of 500 μm in the same manner as that in Example 1, except that a raw material gas SiH_4 containing a doping gas $\text{Ga}(\text{CH}_3)_3$ and a H_2 gas (a ratio of the
10 amounts of gas flow of $\text{SiH}_4 : \text{H}_2 = 1 : 20$, and $\text{Ga}(\text{CH}_3)_3/\text{SiH}_4 = 0.03$) were fed into the raw material gas feed pipe 106 through the energy application device 112 (the plasma reaction chamber) and that the gradual cooling rate of the In solvent 104 was adjusted at $-2^\circ\text{C}/\text{min}$.

15 [0086] The film thickness of the grown Si layer was evaluated by a height difference calculation method and the like, and was about 30 μm . A part of the grown Si layer was examined by secondary mass spectrometry and, as a result, about $2 \times 10^{16}/\text{cm}^3$ to $3 \times 10^{16}/\text{cm}^3$ of Ga was detected in the Si
20 layer.

[0087] Thermal diffusion of P was performed at a temperature of 900°C while POCl_3 served as a diffusion source, an n⁺ layer was formed on the surface of the grown Si layer, and a junction depth in the order of 0.5 μm was achieved. A
25 dead layer of the formed n⁺ layer surface was wet-oxidized,

and was removed by etching, so that a junction depth in the order of $0.2\ \mu\text{m}$ was achieved with a proper surface concentration.

[0088] Finally, collecting electrode (Ti/Pd/Ag (40 nm / 20 nm / $2\ \mu\text{m}$)) / SiN antireflective film (82 nm) was formed on the n^+ layer, a back electrode was formed on the back of the substrate and, therefore, a solar cell was prepared.

[0089] With respect to the thus prepared thin-film single-crystal Si solar cell, the I-V characteristic under AM 1.5 ($100\ \text{mW}/\text{cm}^2$) light irradiation was measured. As a result, the open-circuit voltage was 0.61 V, the short-circuit photocurrent was $34\ \text{mA}/\text{cm}^2$ and the fill factor was 0.78 at a cell area of $4\ \text{cm}^2$ and, thereby, the energy conversion efficiency of 16.2% was derived.

[0090] As described above, according to the preferred embodiments of the present invention, the raw material can be continuously supplied and the decomposition efficiency of the raw material gas and/or the gas containing the dopant can be increased in the liquid phase growth method for a silicon crystal. Consequently, the throughput of the crystal growth can be improved. Furthermore, the present invention is suitable as the mass production method for a device require to be thick, in particular, a solar cell.

[0091] While the present invention has been described with reference to what are presently considered to be the

preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. On the contrary, the invention is intended to cover various modifications and equivalent arrangements included within
5 the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.